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Decoupling of the superconducting and magnetic/structural phase transitions in electron-doped $BaFe_2As_2$

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Study and comparison of over 30 examples of electron-doped $BaFe_2As_2$ for transition metal (TM)=Co, Ni, Cu, and (Co/Cu mixtures) have led to an understanding that the suppression of the structural/antiferromagnetic phase transition to low-enough temperature in these compounds is a *necessary* condition for superconductivity but not a *sufficient* one. Whereas the structural/antiferromagnetic transitions are suppressed by the number of TM dopant ions (or changes in the c axis) the superconducting dome exists over a limited range of values of the number of valence electrons added by doping (or values of the a/c ratio). By choosing which combination of dopants is used we can change the relative positions of the upper phase lines and the superconducting dome, even to the extreme limit of suppressing the upper structural and magnetic phase transitions without the stabilization of a lower-temperature superconducting dome.

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The discovery of superconductivity in the LaFeAsO (Ref. 1) and $BaFe_2As_2$ (Ref. 2) systems has lead to a renaissance of interest in transition-metal (TM)-based superconductivity. Both of these systems manifest substantial T_c values when the structural/antiferromagnetic phase transitions are sufficiently suppressed by substitution on the alkali-earth transition-metal and/or oxygen site. Although the systematic studies of F and K dopings have been difficult due to problems in controlling and assessing stoichiometry, transition-metal doping, especially of the $BaFe_2As_2$ system, has been tractable and quantifiable.

In the case of $Ba(Fe_{1-x}Co_x)_2As_2$ a comprehensive and highly reproducible, $T(x)$ phase diagram has been determined[3] and confirmed/reproduced by several groups.[4–6] The structural phase transition is suppressed by roughly 15 K per atomic percent Co and increasingly separates from the lower magnetic phase transition as more Co is added.[3,4,7,8] For intermediate doping levels, superconductivity has been observed to strongly interact with the magnetic order and fluctuations in the antiferromagnetically ordered orthorhombic state.[7] For higher Co-doping levels both the structural and antiferromagnetic phase transitions are suppressed and superconductivity occurs in the tetragonal phase. These data are all consistent with the idea that superconductivity is stabilized when the tetragonal phase is brought to "low-enough" temperatures by perturbing the parent compound. This may be associated with reducing the size of the orthorhombic distortion and ordered moment "enough" or bringing the magnetic fluctuations associated with the tetragonal phase to "low-enough" temperatures. Superconductivity does not require the complete suppression of the orthorhombic/antiferromagnetic phase, just its suppression to an adequately low temperature.[3–6]

There is a clear correlation between the upper (structural and magnetic) phase transitions and the lower temperature, superconducting phase, but, to date, it is a qualitative one at best. In this Rapid Communication we have studied over 30 samples of electron-doped $BaFe_2As_2$ where the electron doping is coming from $3d$ transition-metal substitutions on the Fe site. We have grown and examined single crystalline samples of the $Ba(Fe_{1-x}TM_x)_2As_2$ system for TM=Co, Ni, Cu, and (Co/Cu mixtures) and find that whereas the suppression of the upper structural phase transitions is a *necessary* condition for low-temperature superconductivity, it is not a *sufficient* one. This distinction can be understood by our observation that whereas the upper transitions appears to be suppressed by the number of impurity atoms substituted for Fe (or the change in the crystallographic c axis) the location and extent of the superconducting dome scale with the number of additional valence electrons, one for each Co, two for each Ni, and three for each Cu atom (naively assuming a similar state, e.g., TM^{2+} for all TM) or the change in the ratio or the crystallographic a axis to c axis. By choosing which combination of dopants is used, we can change the relative positions of the upper phase lines and the superconducting dome, even to the extreme limit of suppressing the upper structural and magnetic phase transitions without the stabilization of a low-temperature superconducting dome.

Single crystals of $Ba(Fe_{1-x}TM_x)_2As_2$ for TM=Ni, Cu, and (Co/Cu mixtures) were grown in a similar manner as the $Ba(Fe_{1-x}Co_x)_2As_2$ compounds.[3] Actual doping levels (rather than nominal) were determined via wavelength-dispersive spectroscopy analysis using an electron probe microanalyzer of a JEOL JXA-8200 electron microprobe and are denoted as x_{WDS}. Powder x-ray diffraction spectra with Si standard were measured using a Rigaku MiniFlex and unit-cell parameters were extracted using "UNITCELL" analysis package. Although we attempted to synthesize similar doping levels of the various Co, Ni, Cu, and Co/Cu series by using identical nominal values, experimentally determined doping levels revealed slightly different actual values of incorporation of these different TM dopants. Electrical resistivity measurements were made using a standard four-probe configuration and Quantum Design physical property measurement system and magnetic property measurement system units to provide the temperature/field environment. Although single crystals can be shaped into well-defined geometries, the $AEFe_2As_2$ materials are prone to exfoliation along the c axis that can lead to spurious resistivity values due to poorly defined current path lengths and cross sections.[3,9,10] For this reason normalized

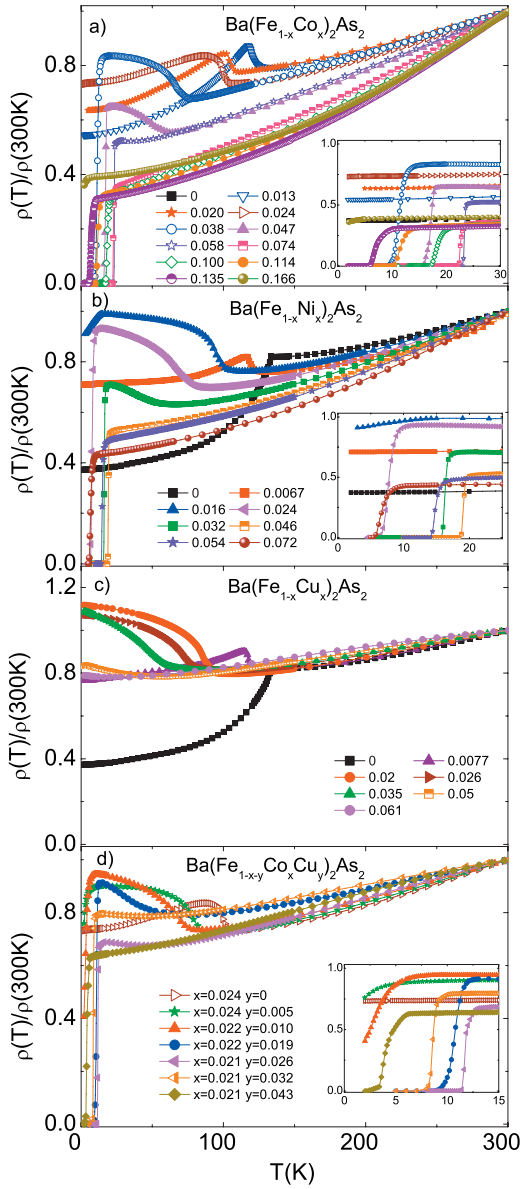

FIG. 1. (Color) The temperature-dependent resistivity, normalized by room-temperature value, for electron-doped $Ba(Fe_{1-x}TM_x)_2As_2$ (TM=Co, Ni, Cu, and Co/Cu) series: (a) $Ba(Fe_{1-x}Co_x)_2As_2$.[3] Inset: low-temperature data for $Ba(Fe_{1-x}Co_x)_2As_2$ (b) $Ba(Fe_{1-x}Ni_x)_2As_2$. Inset: low-temperature data for $Ba(Fe_{1-x}Ni_x)_2As_2$, (c) $Ba(Fe_{1-x}Cu_x)_2As_2$, (d) $Ba(Fe_{1-x-y}Co_xCu_y)_2As_2$. Inset: low-temperature data for $Ba(Fe_{1-x-y}Co_xCu_y)_2As_2$.

resistivity values are plotted. Although only resistivity data are presented in this Rapid Communication, detailed magnetization and specific-heat data have also been collected; as in the case of $Ba(Fe_{1-x}Co_x)_2As_2$,[3] these thermodynamic data further support the $T(x)$ phase diagrams we infer from transport data.

Figures 1(a) and 1(b) present the temperature-dependent normalized resistivity for $Ba(Fe_{1-x}TM_x)_2As_2$ system for TM=Co and Ni, respectively. For each TM dopant there is a clear suppression (and separation) of the upper transitions with increasing x and superconductivity is clearly stabilized once the structural/magnetic phase transitions are sufficiently suppressed and exists in both the orthorhombic/antiferromagnetic phase as well as in the tetragonal one at high dopings.[3,7,11] Although $BaCu_2As_2$ itself appears to be a relatively innocuous compound,[12,13] the $Ba(Fe_{1-x}Cu_x)_2As_2$ series [Fig. 1(c)] reveals a key difference: although the signature of the structural/antiferromagnetic phase transition is suppressed in a manner similar to that seen for TM=Co and Ni, there is no superconductivity found for any x value tried (up to values six times greater than the $x=0.061$ shown). This means that the signatures of the orthorhombic/antiferromagnetic transitions are not truncated by superconductivity and can be observed to fade as x is increased.

In order to clarify the effect of Cu as a dopant (i.e., is it particularly pernicious to superconductivity or is it essentially part of a continuum that contains Co and Ni dopants as well) we studied a $Ba(Fe_{1-x-y}Co_xCu_y)_2As_2$ series ($x\sim0.022$ and $0\leq y<0.05$). Figure 1(d) presents selected normalized resistivity plots for this series. As can be seen in Fig. 1(a), a Co doping of $x=0.024$ is insufficient to induce superconductivity, but additional doping by Cu [Fig. 1(d)] can indeed induce superconductivity. These data clearly show that Cu is not inherently antithetical to the superconducting state and that there may well be a deeper and more profound realization to be made based on these data.

The data presented in Fig. 1 can be summarized in a T-x phase diagram. The transition temperature values for the upper structural and magnetic phase transitions were inferred from these data in manner similar to that used in Ref. 3 and subsequently supported by microscopic measurements.[7,8] For the higher Cu concentrations ($x=0.05$ and 0.061) the resistive features become so broad that the error bars associated with the determination of the upper (only detectable) transition are defined by the temperature of the resistance minima on the high side and the temperature of the inflection point on the low side. Figure 2(a) displays the T-x phase diagram for each of the $Ba(Fe_{1-x}TM_x)_2As_2$ (TM=Co, Ni, Cu, and Co/Cu) series. Whereas the suppression of the upper phase transitions for each of these different series appears to depend on x in a similar manner, the occurrence of superconductivity is not well described by this parametrization. Superconductivity is found for a wide range of Co-doping values, a narrower range of Ni doping values, and an even narrower range of Cu doping values [in the $Ba(Fe_{1-x-y}Co_xCu_y)_2As_2$ series].

There is, of course, a second way of plotting these data: transition temperature as a function of extra conduction electrons added by the dopant, i.e., grossly assuming the validity of a rigid band approximation for these dopants. For TM=Co, the number of impurity atoms, x, per TM site is the same as the number of extra valence electrons, e, per TM site. When TM=Ni or Cu, this is not the case. A second parametrization of the data inferred from Fig. 1 is shown in Fig. 2(b): a T-e phase diagram, where e is the number of extra valence electron added per Fe/TM site (for the case of Co $e=x$, for the case of Ni $e=2x$, and for the case of Cu $e=3x$). This parametrization does a much better job of unifying the superconducting domes of these compounds but clearly does a much poorer job of capturing the physics of the suppression of the upper structural/antiferromagnetic phase transitions.

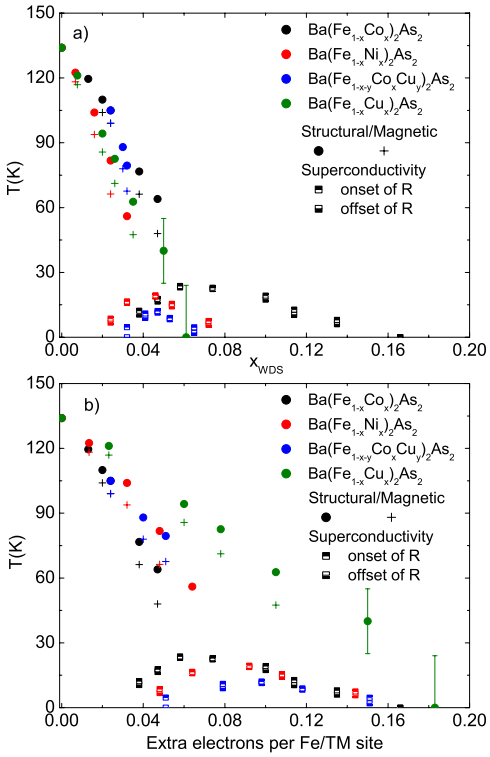

FIG. 2. (Color online) (a) Transition temperature as a function of the number of substitutional transition-metal ions per Fe site; (b) transition temperature as a function of extra electrons contributed by TM substitution per Fe site. For both plots the transition temperatures were determined in a manner similar to that described in Ref. 3 and the text.

It should be noted that whereas the assumption that Ni (and Co) doping can shift the Fermi level upward, [because of the higher valence electron count in Ni^{2+} ($3d^8$) compared to Fe^{2+} ($3d^6$)] (Ref. 14) is generally accepted, the state of Cu impurities and their effect on the Fermi level and band structure is less clear. Recent Hall and thermoelectric power data[15] are consistent with Cu electron doping the $BaFe_2As_2$ at a rate that is clearly larger than Co doping, so the assumption that, for low doping levels, Cu is adding three valence electrons per atom seems plausible.

Although x and e are intuitive (and relatively easy to determine) parameters, they are certainly not unique ones. Figures 3(a)–3(d) demonstrate that whereas the c-lattice parameter variation is similar to x, the variations in the a-lattice parameter, the volume and the a/c ratio do not show universal behavior when plotted as a function of x. This means that the statement that the upper structural and antiferromagnetic phase transitions scale with x is equivalent (experimentally) with the statement that they scale with the variation in the c-lattice parameter.

Further examination of Figs. 3(a)–3(d) reveals that whereas a change in parameter from x to e will not lead to a collapse of the data for a/a_0, c/c_0, or V/V_0 onto a universal curve, the variation in the a/c data appears promising, showing variations in x that differ by factors of 2 and 3. Figure 3(e) plots the variation in a/c as a function of e. As clearly shown, a/c and e are experimentally equivalent variables (for $3d$ TM electron doping) as well.

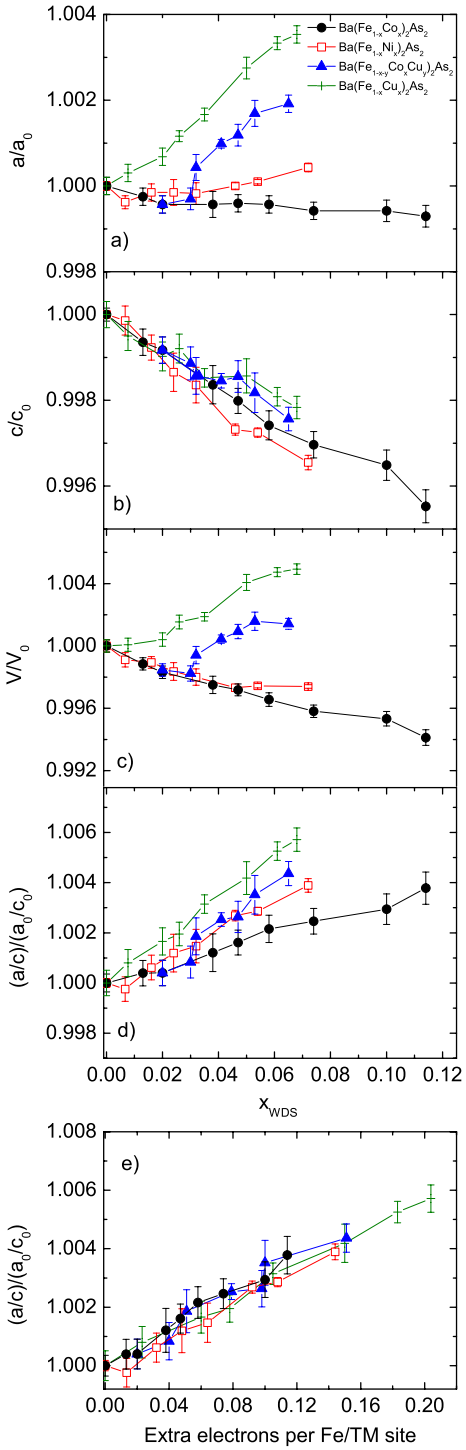

FIG. 3. (Color online) Normalized structural parameters measured at ~300 K. (a) a/a_0, (b) c/c_0, (c) V/V_0, and (d) $(a/c)/(a_0/c_0)$ as a function of transition-metal doping, x, and (e) $(a/c)/(a_0/c_0)$ as a function of extra conduction electrons, e. (a_0 =3.9621 Å and c_0=13.0178 Å).

One obvious parameter that has not been examined in this study is the As-Fe-As bonding angle. Unfortunately this was not extracted from our diffraction data, and given that the location of the As site is free to vary, it is hard to model. Future measurements will have to determine whether this angle is related to either x or e.

The phase diagrams in Fig. 2 provide graphic evidence that the structural/antiferromagnetic phase transitions and the occurrence of superconductivity depend on different parameters for electron doping via TM substitution: number of impurities (change in *c*-axis parameter) and number of additional electrons (a/c ratio), respectively. This difference allows for the decoupling of these transitions and the ability to realize that the suppression of the structural/antiferromagnetic phase transition to low-enough temperature is a *necessary* condition for superconductivity but not a *sufficient* one. The data from the $Ba(Fe_{1-x}Cu_x)_2As_2$ series clearly demonstrate that if too many electrons are added in the process of suppressing the structural/antiferromagnetic phase transition the superconducting dome can be overshot; i.e., by the time the structural/antiferromagnetic transition is suppressed enough, too many conduction electrons have been added and window for superconductivity has been missed. A closer examination of Fig. 2(b) brings this point even further into focus: although the superconducting domes for the $Ba(Fe_{1-x}Co_x)_2As_2$, $Ba(Fe_{1-x}Ni_x)_2As_2$, and $Ba(Fe_{1-x-y}Co_xCu_y)_2As_2$ series are essentially indistinguishable on the higher doping side, they differ, somewhat, on the lower doping side. This difference would be consistent with needing to bring the upper transition to low-enough temperature to allow the superconductivity to turn on: $Ba(Fe_{1-x}Co_x)_2As_2$ with its more rapidly decreasing upper transitions manifest superconductivity at slightly lower *e* values than the Ni-doped or Cu/Co-doped series.

The observation that the upper transitions depend on either the number of TM dopant atoms added, *x*, or, equivalently, the change in the *c*-axis dimension, leads to two differing scenarios for what physical parameter controls this suppression. If *x* is the salient parameter, then the upper transitions are controlled by local physics such as vacancies on the Fe sublattice or the disruption of very short-range fluctuations. On the other hand if the size of the *c*-axis parameter is the salient variable, then details of band structure (nesting or not) or degree of As-As bonding across the Fe plane would be more likely to control/affect the value of the upper transition temperatures.

The observation that the superconducting dome is delineated by a minimum and maximum number of extra conduction electrons (or possibly a/c ratio) provides a clear theoretical constraint/test for current theories of superconductivity in these fascinating, complex, and potentially useful[16] compounds.

In conclusion, the study and comparison of over 30 examples of electron-doped $Ba(Fe_{1-x}TM_x)_2As_2$ have led to an understanding that the suppression of the structural/antiferromagnetic phase transition to low-enough temperature in these compounds is a *necessary* condition for superconductivity but not a *sufficient* one. Whereas the structural/antiferromagnetic transitions are suppressed by the number of TM dopant ions (or changes in the *c* axis) the superconducting dome exists over a limited range of values of *e*, the number of electrons added by doping (or values of the a/c ratio). As clearly shown by the $Ba(Fe_{1-x}Cu_x)_2As_2$ series, if too many electrons are added per TM dopant, then the window for superconductivity can be completely missed. Further work, including 4*d*- and 5*d*-TM-based electron dopings as well as a more detailed study of the state of Cu and its effects on the Fermi level and band structure, will have to be carried out to see how general this decoupling of the structural and superconducting transitions is and perhaps help resolve which parametrization is the physically most relevant.

Note added in proof. Further work on TM=Rh and Pd doping[17] sheds further light on the effects of electron doping and also indicates that *x* and *e* are the salient variables for universal phase diagrams such as shown in Fig. 2.

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